ESE Studies of Pristine Paramagnetic Species of C_{60} Powder Samples

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Paramagnetic centers in pristine polycrystalline C_{60} samples are investigated at room temperature using continuous wave electron paramagnetic resonance (CW-EPR) and electron spin−echo spectroscopy. Two paramagnetic species, with same measured g-values, are separated using echo-detected EPR and the PEANUT pulse scheme. Electron-spin nutation frequencies for both species are measured using the latter technique. For the doublet species, usually observed by CW-EPR, nutation frequency is 7.5 MHz. The second species, with a nutation frequency of 10.4 MHz, is a spin triplet. This species is solely revealed by pulse methods and corresponds to dipolar coupling of C_{60} paramagnetic centers located at the diagonals of the fullerene fcc lattice.

Introduction

Discovery of C_{60} fullerenes[1] and the possibility of production of significant quantities[2] have promoted several studies of this allotrope form of carbon. Reduction of C_{60} fullerenes up to six electrons stimulated search in the synthesis of chemical derivatives and investigation of their properties.[3] Some alkali-metals doped C_{60} have superconducting attributes.[4] Magnetic and photochemical properties have also been observed in fullerene doped compounds.[5]

The various valences of C_{60} and the possibility of binding to radicals producing paramagnetic adducts make electron paramagnetic resonance (EPR) a suitable technique for the study of these compounds and their reactions.

The C_{60} molecule is a neutral one. No EPR lines in solid pristine samples are expected. However, even high-purity powders of C_{60} from several sources, commercially available or homemade, show EPR lines around $g = 2.0028$ with line width about 0.12 mT at room temperature. Sharp signals have been observed in several C_{60} samples and derivatives. In solid pristine samples this signal was attributed to a C_{60} cation doublet ($S = 1/2$) species.[6] Triplet species ($S = 1$) were also observed in powder C_{60} by continuous wave electron paramagnetic resonance (CW-EPR). These species are attributed to a photon-assisted reaction with molecular oxygen of the air.[7] Reaction of oxygen with radicals generated by irradiation on fullerene in toluene solution confirms the influence of oxygen in fullerene paramagnetic species.[8] Electron spin−echo measurements of polycrystalline C_{60} below 120 K were able to identify one paramagnetic center, though three centers are observed at different CW-EPR microwave powers.[9]

Fullerene powder is largely used as starting material for synthesis of new chemical complexes. Knowledge on paramagnetic centers already present in the powder is certainly valuable for the EPR analysis of fullerene derivatives.

In this work, echo-detected EPR and the recently introduced PEANUT pulse scheme[10] are used to get deeper insight on the paramagnetic species of pristine fullerene powder. The PEANUT experiment is a two-pulse spin−echo scheme where the refocusing second pulse is a high-turning angle pulse of length T divided into two parts of length t and $T - t$ with opposite phases of 0 and π respectively. This technique is based on the proportionality between the transition moment and the frequency at which the electron nutates under resonant microwave radiation. In this pulse sequence the transient electron spin nutation frequencies are measured via an electron spin−echo detected rotary echo. Nutation frequencies, are related to g-values and electron-spin multiplicity and can be used to identify species with or without hyperfine interactions.[10] A 2D-PEANUT experiment was performed correlating echo amplitude as a function of time and external magnetic field positions. In these experiments, as the total length of the pulse sequence is kept constant, the influence of relaxation processes is the same during all data acquisition.

Experimental Section

Two commercial fullerene samples (Southern Chemical Co. and Aldrich) and one homemade were used in this work. The former (>99% pure) was used as purchased. The Aldrich sample, purchased as fullerite, was further purified using a chromatography column of SiO_2/Elorit.[11] The homemade sample was obtained by an arc-discharge method and further purified. A standard aliquot of 25 mg was used in all experiments.

Measurements were carried out on a Bruker ESP-380FT/CW X-band spectrometer. Echo-detected EPR measurements were performed using pulses of 56 and 112 ns. The 56 ns preparation pulse corresponds to a 0.64 mT excitation bandwidth. This is enough to cover the entire EPR width and minimize spectral diffusion. Phase memory times were obtained from two-pulse echo decay in a time window of 123 μs. Echo decays were fitted using a spectrometer internal routine. In the PEANUT experiment a 2408 ns second pulse was used 400 ns after the 56 ns pulse. Spectra were processed using the Bruker WIN-EPR software.

Results

The CW-EPR spectrum of C_{60} at room temperature, shown in Figure 1, consists of an intense line at $g = 2.0026 \pm 0.0002$

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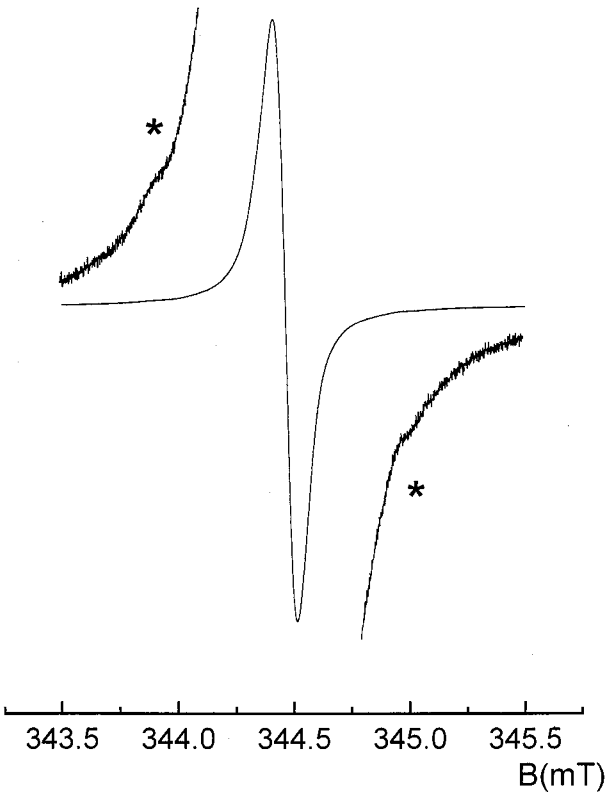

Figure 1. Powder C_{60} pristine sample CW-EPR at room temperature. Microwave power is 0.1 mW and modulation amplitude is 0.5 G. Asterisks indicate the triplet species lines at high gain.

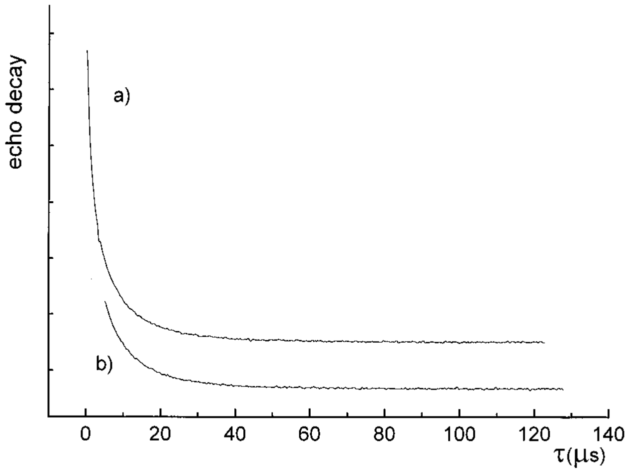

Figure 2. Two-pulse echo decay observed for pristine C_{60} powder sample. (a) 0.4 μs initial pulse separation and (b) 5 μs initial pulse separation.

flanked by two small lines. These lines are better observed at high gain. This spectrum is observed in the three samples under study, with different relative intensities, indicating distinct concentration of the paramagnetic species. This is confirmed by differences found in phase memory times, which depend on species concentration.[12]

Echo decays for the Southern Chemicals sample, obtained with initial pulse separations of 0.4 and 5.0 μs, are shown in Figure 2. Decays are fitted to two exponential functions. Fitting data is summarized in Table 1. In both cases, although phase memory times are approximately the same, exponential amplitudes depend on the initial pulse separation, suggesting the existence of distinct paramagnetic species contributing to phase relaxation. Moreover, the echo decay with long pulse separation can be fitted to only one exponential. The echo-detected EPR method was then used to select distinct paramagnetic species. Two experiments, shown in Figure 3, were performed: echo intensity was detected with pulse separations of 0.4 and 5.0 μs, respectively, to favor one species over the other. External magnetic field was varied in 0.02 mT steps. The results indicate two EPR species, with the same g-values as measured by CW-EPR. However, for the largest pulse separation, the echo detected spectrum reveals a splitting of about 0.25 mT. Line width is slightly larger than that measured by CW-EPR due to the use of the spectrometer sampling digitizer instead of an integrator for echo detection.

TABLE 1: Echo Decay Fitting Parameters

pulse separation	double exponential[a]	single exponential
0.4 μs	$T_{m1} = (1.27 \pm 0.02)\ \mu$s $A_1 = (6.18 \pm 0.04) \times 10^3$ $T_{m2} = (8.60 \pm 0.06)\ \mu$s $A_2 = (4.87 \pm 0.04) \times 10^3$	do not fit
5 μs	$T_{m1} = (1.3 \pm 0.2)\ \mu$s $A_1 = (0.30 \pm 0.03) \times 10^3$ $T_{m2} = (8.9 \pm 0.2)\ \mu$s $A_2 = (2.9 \pm 0.2) \times 10^3$	$T_m = (8.5 \pm 0.2)\ \mu$s $A = (3.0 \pm 0.2) \times 10^3$

[a] A stands for exponential amplitude.

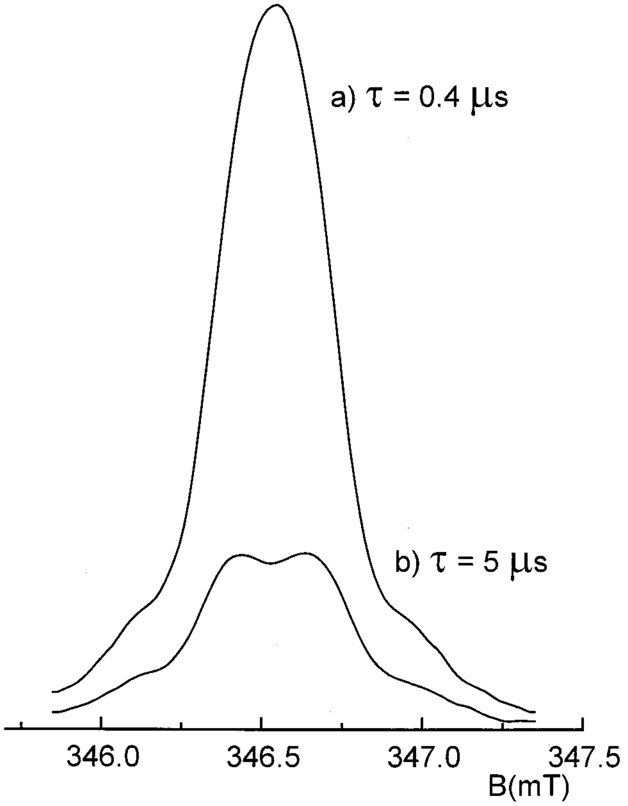

Figure 3. Echo-detected EPR of C_{60} powder sample. (a) Spectra obtained with 0.4 μs pulse separation and (b) with 5 μs pulse separation.

Further investigation on these paramagnetic species was carried on by a PEANUT experiment. Figure 4 shows a contour plot of the absolute valued Fourier transformed time data, as well as two cross-sections at 7.5 and 10.4 MHz. The cross-sections, as pointed out in ref 10, are nutation frequency selective EPR spectra. They clearly correspond to the spectra observed by the echo-detected EPR method.

Discussion

In electron spin−echo experiments, spin magnetization is turned by the resonant microwave pulse magnetic field $\boldsymbol{B}_1$,

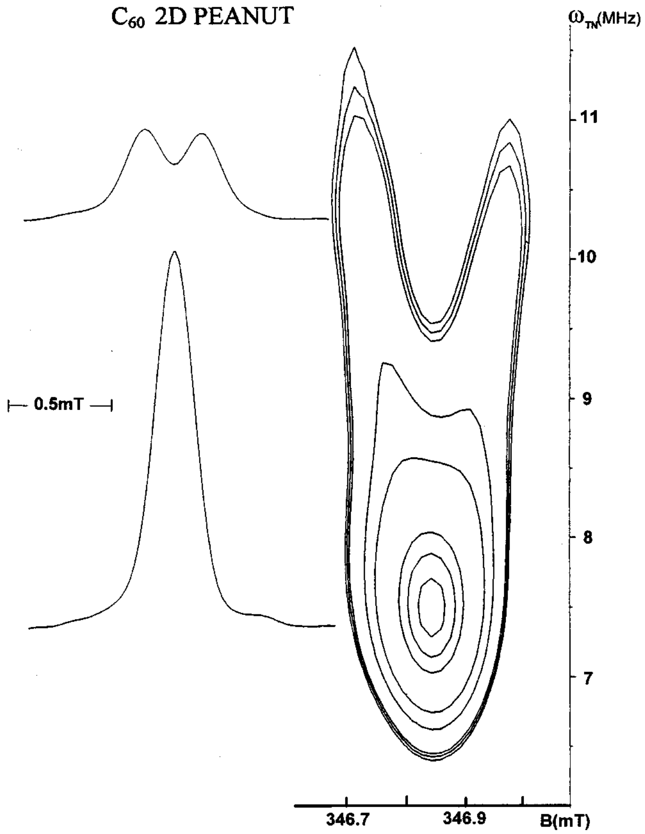

Figure 4. 2D-PEANUT contour plot of the absolute valued Fourier transformed data of C_{60} powder sample. Cross-sections at two nutation frequencies are shown.

depending on the magnitude of the magnetic moment μ associated to the spins. This gives a characteristic nutation frequency that depends on μ and the transition involved. The $\boldsymbol{B}_1$ field required for a $\pi/2$ turning angle for an $S = 1$ species is $\sqrt{2}$ smaller than the field required for an $S = 1/2$ species. This factor is approximately the ratio of the nutation frequencies measured in the present PEANUT experiment, indicating that the higher nutation frequency species is a triplet species with zero-field splitting of about 0.25 mT.

The triplet species corresponding to the lines flanking the sharp signals in CW-EPR spectra of pristine C_{60} samples have been attributed to dimmers formed by two doublet species.[2] Using a point-dipole approximation where the exchange and anisotropy terms are neglected, the distance r between the two interacting centers can be evaluated from[13]

$$D_{dd} = 0.65\, g^2/r^3$$

where D_{dd} corresponds to half of the zero-field splitting (1.2 mT) of the triplet species. The factor 0.65 applies to distances in Angstroms and D_{dd} in units of cm^{-1}. This equation yields $r = 16.7$ Å. As the C_{60} diameter is 7.1 Å, coupling most probably occurs between paramagnetic centers located at opposite sides of two adjacent C_{60} buckyballs. On the other hand, a zero-field splitting of 0.25 mT measured by ESE corresponds to a distance of about 28 Å. Interacting centers, in this case, should be localized in buckyballs belonging to a face diagonal or/and to the diagonal of the fcc C_{60} unit cell. Resolution precludes a clear distinction between these two situations. Interaction between C_{60} balls located at the cube edge and the center of the cube face are not observed in ESE experiments, indicating, as pointed out in ref 7, that electrostatic and steric hindrances inhibit the formation of doublet species at the center of the cube face.

Conclusions

EPR electron spin−echo methods reveal two distinct paramagnetic species contributing to the signal of pristine C_{60} samples at room temperature. Triplet species resulting from coupling between radicals at the diagonals of the C_{60} unit cell are clearly observed allowing measurement of their zero-field interaction. The PEANUT experiment revealed to be a deciding pulse technique to investigate radicals in fullerene materials.

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References and Notes

(1) Kroto, H. W.; Health, I. R.; O'Brian, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(2) Krätschmer, M. J.; Murphy, D. W.; Fleming, R. M.; Tycko, R.; Ramirez, A. P.; Siegrist, T.; Dabbagh, G.; Barret, S. E. *Nature* **1990**, *347*, 3546.

(3) Khaled, M. M.; Carlin, R. T.; Trulove, P. C.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1994**, *116*, 3465.

(4) Hebard, A. F.; Rosseninsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T.; Ramirez, A. P.; Kortan, A. R. *Nature* **1991**, *350*, 600.

(5) (a) Stephens, P. W.; Cox, D.; Lauher, J. W.; Mihaly, L.; Wiley, J. B.; Allemand, P. M.; Hirsch, A.; Holczer, K.; Li, Q.; Thompson, J. D.; Wudl, F. *Nature* **1992**, *335*, 331. (b) Jehoulet, C.; Bard, A. J.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 5456.

(6) Stankowski, J.; Kempinski, W.; Koper, A.; Martinek, J. *Appl. Magn. Reson.* **1994**, *6*, 145.

(7) Colligiani, A.; Taliani, C. *Chem. Mater.* **1994**, *6*, 1633.

(8) Hwang, Y. L.; Yang, C. C.; Hwang, K. C. *J. Phys. Chem.* **1997**, *101*, 7971.

(9) Hoffmann, S. K.; Hilczer, W.; Kempinski, W.; Stankowski, J. *Solid State Comm.* **1995**, *93*, 197.

(10) Stoll, S.; Jeschke, G.; Willer, M.; Schweiger, A. *J. Magn. Reson.* **1998**, *130*, 86.

(11) Dias, G. H. M. *Quimica Nova* **1995**, *18* (6), 592.

(12) Salikhov, K. M.; Tsvetkov, Yu. D. In *Time Domain Electron Spin Resonance*, Kevan, L., Schwartz, R. N., Eds.; John Wiley and Sons: New York, 1979 p 231.

(13) Chasteen, N. D.; Belford, R. L. *Inorg. Chem.* **1970**, *9*, 2805.